Esterification of Several N.N-disubstituted Phthalamic Acids and Testing the Esters as Plastaziers for Poly (Vinyl Chloride) and Poly Styrene

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Abstract

Three N.N-disubstituted phthalamic acids were prepared by allowing phthalic anhydride to react with secondary amines. The prepared phthalamic acids were esterified directly or via their acid chlorides producing good yields of the corresponding esters. Some of the prepared esters were tested as plasticizers for poly (vinyl chloride) and the results were compared with Dioctyl phthalate (DOP), the universal plasticizers for P.V.C Results showed the new esters as effective plasticizers as DOP for PVC. The esters were also tested as plasticizers for polystyrene.

Introduction

Reactions of anhydrides with primary and secondary amines were well-documented (1-3). The reaction is clean, easy, fast, high yield and without any side products. Numerous uses for the phthalamic acid products are reported in literature (4-6). The main use of amic-acid products is their cyclization to the corresponding cyclic imides. The unsaturated cyclic imides are used mainly as monomers or comonomers for polyimide synthesis. Recently, several esters of N-substituted amic acid esters were prepared in our laboratory and used to plasticizer polystyrene and poly(vinyl chloride) (8). The following paper is a similar study in which novel phthalamic esters are prepared and used in plasticization of poly (vinyl chloride) and polystyrene.

Apparatus:

IR spectrum was recorded using PYE UNICAM PU a512, CHN analysis was carried out using Perkin-Elmer CHN-analyser.

Experimental

1. Preparation of N.N-Disubstituted phthalamic acids

Literature procedures were followed (2,4) with few modification. The procedure for preparation of N,N-Dibenzylamine-phthalamic acid will be described as an example.

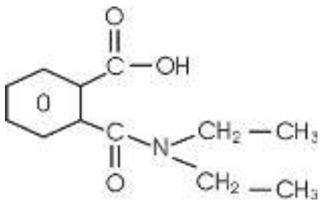
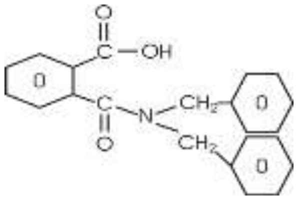
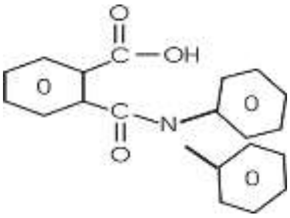
Reaction of phthalamic anhydride with ibenzylamine

In around bottom flask (100 ml) was dissolved 10 g (0.06 mole) of phthalic anhydride in 40 ml of acetone with stirring magnetically. A dropping funnel was charged with 8.5 ml (0.06 mole) of dibenzylamine and placed on top of the flask. The amine was allowed to add to the flask dropwise while stirring , a white precipitate was formed. The precipitate was filtered, washed with dilute (5%) HCl and dried.

The product was recrystallized from n-hexane and the crystals showed a m.p of 157-159^{0}C. The percent yields was 78%. Following the above procedures several-N,N-disubstituted phthalamic acids were prepared.

Table 1 lists the physical properties of three of the prepared phthalamic acids.

Table 1. physical properties and yield of the prepared phthalamic acid

Structure	**Name**	**M.P C^0**	**% yield**
	N,N-diethyl phthalamic acid	152-154	87
	N,N-dibenzyl phthalamic acid	157-159	78
	N,N-diphenyl phthalamic acid	140-142	90

Preparation of Esters from the prepared phthalamic acids
Preparation of Ethyl N,N-(diethyl) phthalamate

A) Preparation of N,N-(diethyl phthalamoyl) chloride [(9)]

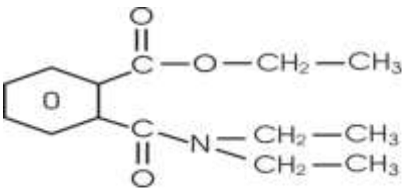
In a two necked round bottom flask (200 ml) was placed 10 g (0.04 mole) of N,N-(diethyl) phthalamic acid. Athionyl chloride, 0.6 ml (0.08 mole) was placed in a dropping funnel, and protected with $CaCl_2$ drying tube. The flask was provided with a reflux condenser, a steam bath, and a magnetic stirrer. The thionyl chloride was allowed to add dropwise to the flask while stirring and heating, the color was changed to yellow-brown the reflux was continued for another hour. The apparatus was changed to distillation apparatus where by the unreacted thionyl chloride distilled off. The residue (acid chloride) was solidified at room temperature and used in step (B) without further purification.

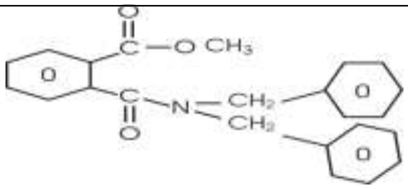
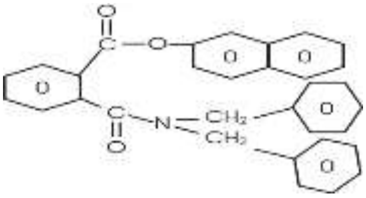
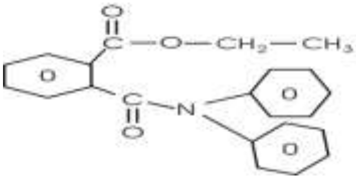
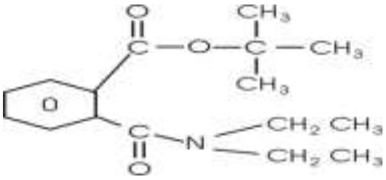
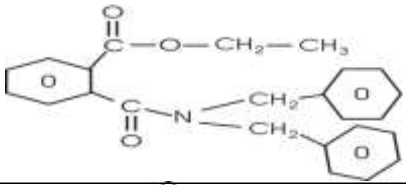
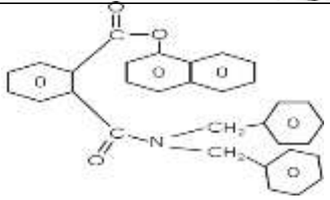
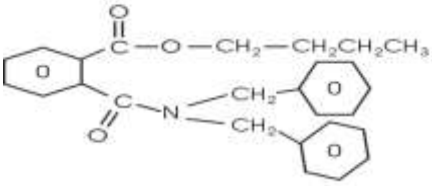
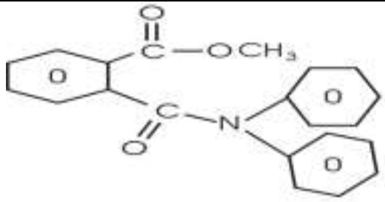
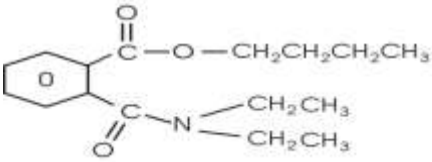
B) Reaction of N,N-(diethyl) phthalamoyl chloride with Ethanol

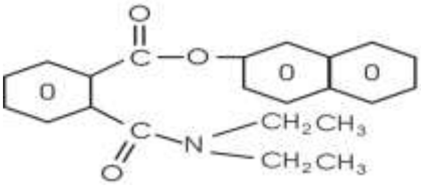
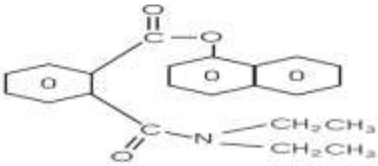
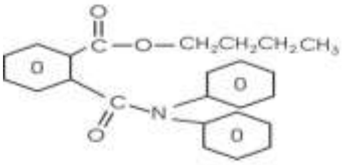
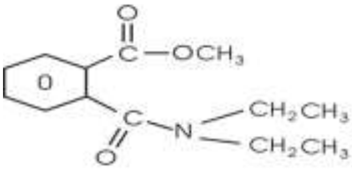
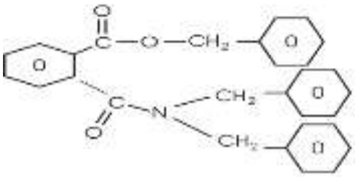
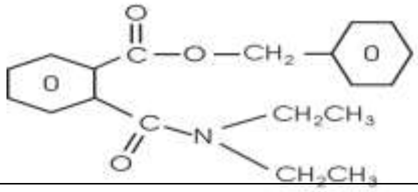
Ethanol (10ml) was added to the product residue in the round bottom in (A) and refluxed for two hours. The mixture was then added to (30ml) of distilled water placed in a saperatory funnel. The mixture was shaked and allowed to settle. Two layers were formed, the lower aqeous layer was extracted a couple of times with (10ml) of ether. The ether extracts were added to the oily layer, washed with (10ml) of water, and dried with anhydrous $MgSO_4$. The ether was allowed to evaporate, red crystals were left. The product was recrystalized from ccl_4, and pure crystals formed showing m.p of 53-55^{0}c and percent yield was 57.7%.

Following the same procedure several other esters were prepared and their physical points are reported in table II.

Table (2):physical properties and yield of the prepared phthalamate

Ester	**M.P C^0**	**B.P C^0**	**% yield**	**Color of product**
	53-55	__	80	Reddish

Ester	**M.P C^0**	**B.P C^0**	**% yield**	**Color of product**
	103-105	—	62	White
	55-57	—	53	White-gray
	93-95	—	56	Green
	54-56	—	65	Yellow
	106-108	—	40	White
	60-62	—	45	Gray
	105-107	—	61	Gray
	55-57	—	36	Green
	63-65	—	45	Gray

Ester	M.P C^0	B.P C^0	% yield	Color of product
		137-139	57	Violet
	45-47	—	51	Violet
	54-56	—	42	Green
	—	159-161	37	Violet
	110-112	—	30	White
	—	310-312	43	Yellow

Use of the new esters as plasticser for pvc.

Three different motheds were empleyed in order to test some of the prepared esters for plasticisation of poly (vinyl chloride).

Methed A.

one gram of poly (vinyl chloride) was mixed with certain amount of dioctyl phthalate (obtained from the Iraqi plastic company, Zafarania, Baghdad) the unplasticised PVC had a M.wt of 10000 gm/mol, and was dissolved in 15 ml of THF in a 200 ml beaker. A thin film of the viscous solution was prepared and allowed to dry before measuring its softening point. Three different percentages of DOP in PVC were prepared and tested their softening point in order to prepare a standard curve for comparison with effects of the prepared esters.

One gram of the unplasticised PVC was dissolved in 15 ml of THF in a small beaker. In another beaker 0.1 g of the amic ester was dissolved in 5.0 ml of THF. The two solutions were mixed well and used to prepare a thin film on a clean slide of glass. After complete dryness the film was removed and its softening point was determined.

Methed B

Three milliliters of the liquid ester (amic ester) was placed in a conical flask and heated to 130-140^0 C. preweighed amount of powdered PVC was gradually added to the ester with stirring, until a homogenecus mixture was obtained. The mixture was added to water. The solidified material was dried before determining its softening point.

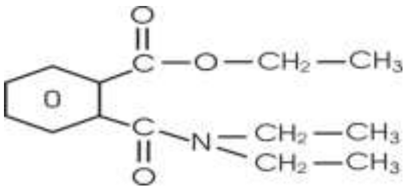
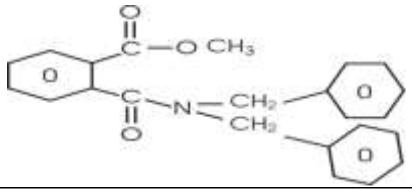
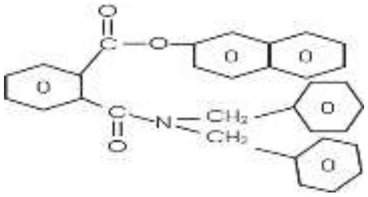
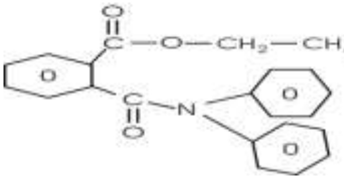
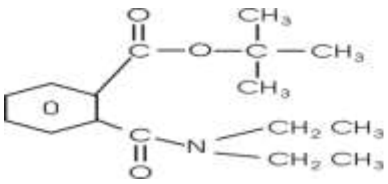
Methed C

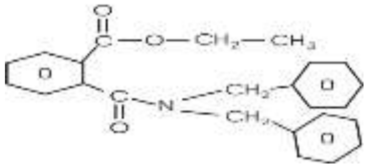
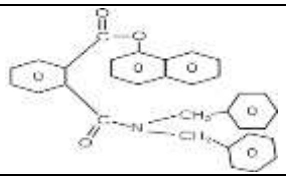
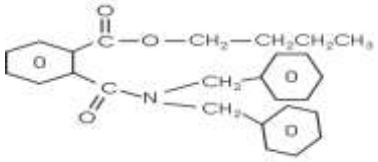
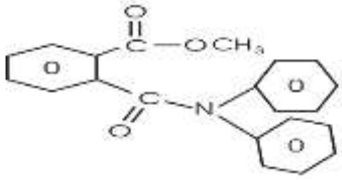
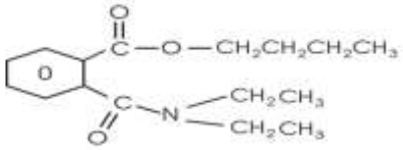
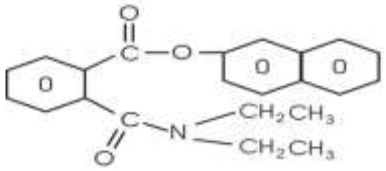
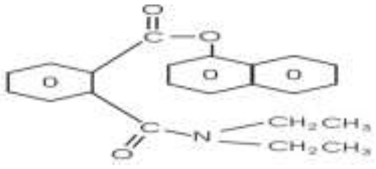
In an agar morter 1.0 g of unplasticised PVC was mixed with the exact weight of one of the prepared amic ester, grounded well until forming a homogemeous mixture; the softening point was determined.

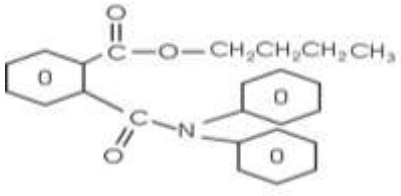
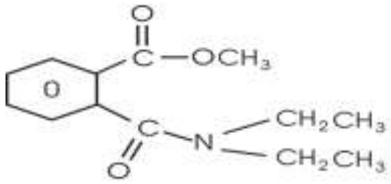
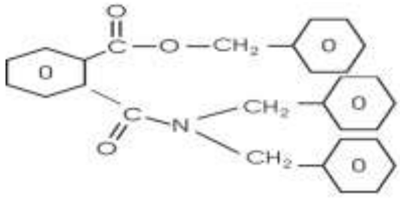
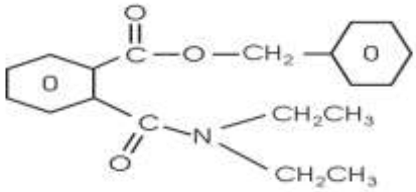
Results and Discassion

Literature procedures were followed to prepare the new N – substitutled phthalamic acids. The reactions were straight forward and the yeilds were high. Table I lists structures names and melting points of the prepared amic acids. It is important to notice that all the employed amines that were allowed to react with phthalic anhydride were secondary amines and not primary. This was to avoid cyclization of the amic acids to from the carresponding imides during heating or treatment with thionyl chloride prior to esterification. The yeilds of the esters obtained by direct reaction of the alcohol with the amic acids using sulfuric acid as catalyst gave low yeilds of the corresponding esters. However, indirect esterification via converting first the amic acids to their corresponding acid chlorides followed by reaction with the alcohols gave fair to good yeilds of the esters. Table II lists the structures, melting points or boiling points, percent yeilds and colours of the perpared esters. Structures of the esters were proved by I.R analysis and hydroxamie acid test of esters. The I.R spectra of the esters in (KBr) showed carbonyl absorptions of the ester and amides. Table III lists major I.R absorptions and Elemental analysis of some of the prepared esters.

Table III Major I.R. Absorption of the prepared Esters and their Elemental Analysis

Ester	V c=0cm^{-1} Ester	V c=0cm^{-1} Amide	C.H.N. Anal					
			Cald %			Found %		
			C	H	N	C	H	N
	1770	1700	67.40	7.83	5.62	67.20	8.10	5.05
	1760	1700	70.50	5.37	3.58	69.54	5.60	4.70
	1755	1700	81.10	5.70	2.95	81.90	6.90	2.90
	1710	1660	76.50	5.50	4.05	77.10	5.70	4.45
	1770	1710	69.31	8.30	5.05	69.80	7.90	6.60

Ester	**V c=0cm^{-1}** Ester	**V c=0cm^{-1}** Amide
	1760	1705
	1760	1690
	1766	1710
	1720	1660
	1760	1705
	1760	1700
	1770	1705

Ester	**V c=0cm^{-1}** Ester	**V c=0cm^{-1}** Amide
	1710	1655
	1765	1700
	1760	1715
	1715	1635

Application of five of the prepared esters as plasticizers for PVC and polystyrene showed them fairly efficent and could be used instead of (Dioctyl phthalamate)(Dop).

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Figures 1 and 2 show the results of such experiments. Up to 30% of the esters were used and mixed with (PVC) and polystyrene as plasticizers

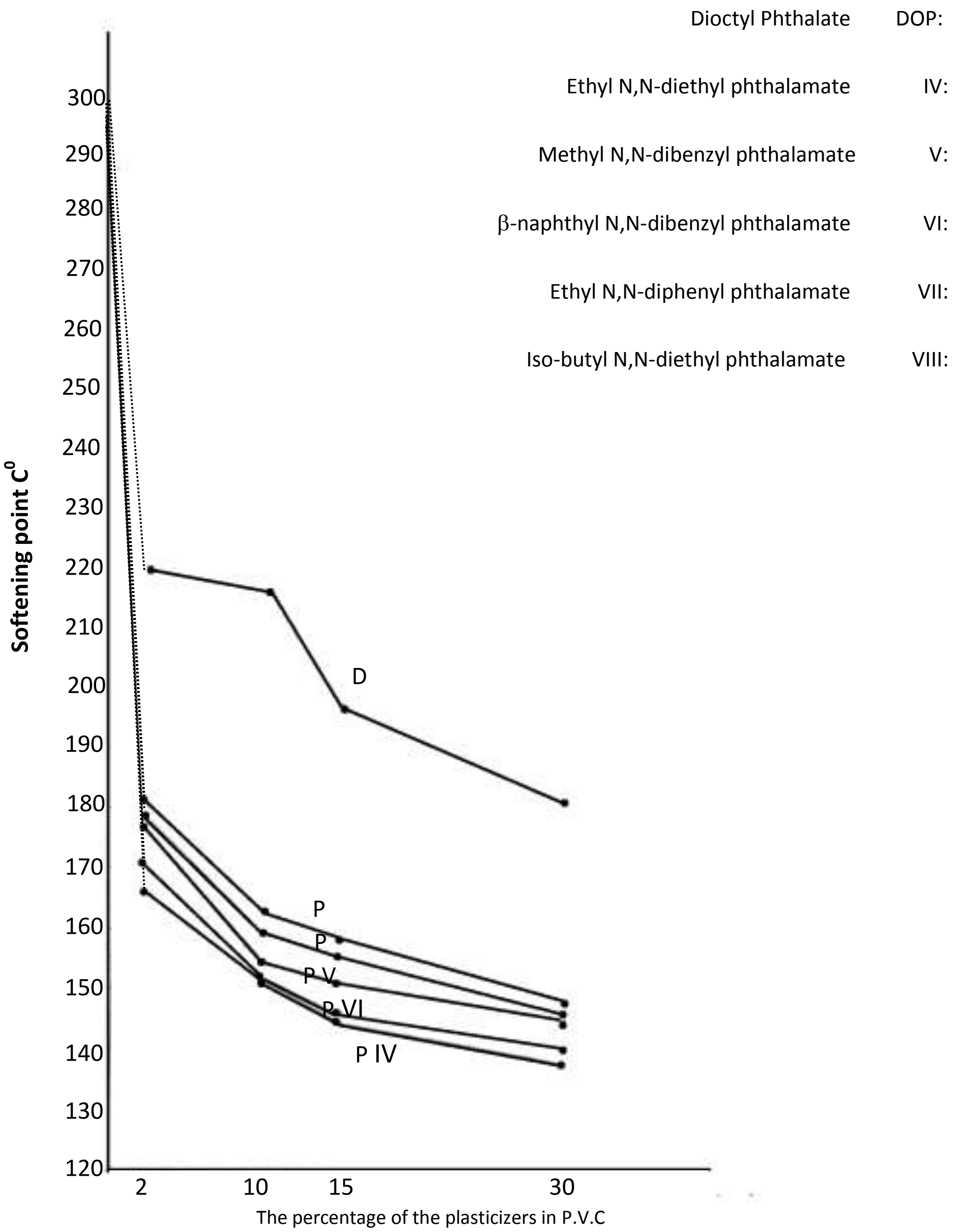

Fig. (1): The effect of the plasticizers to the softening point of P.V.C

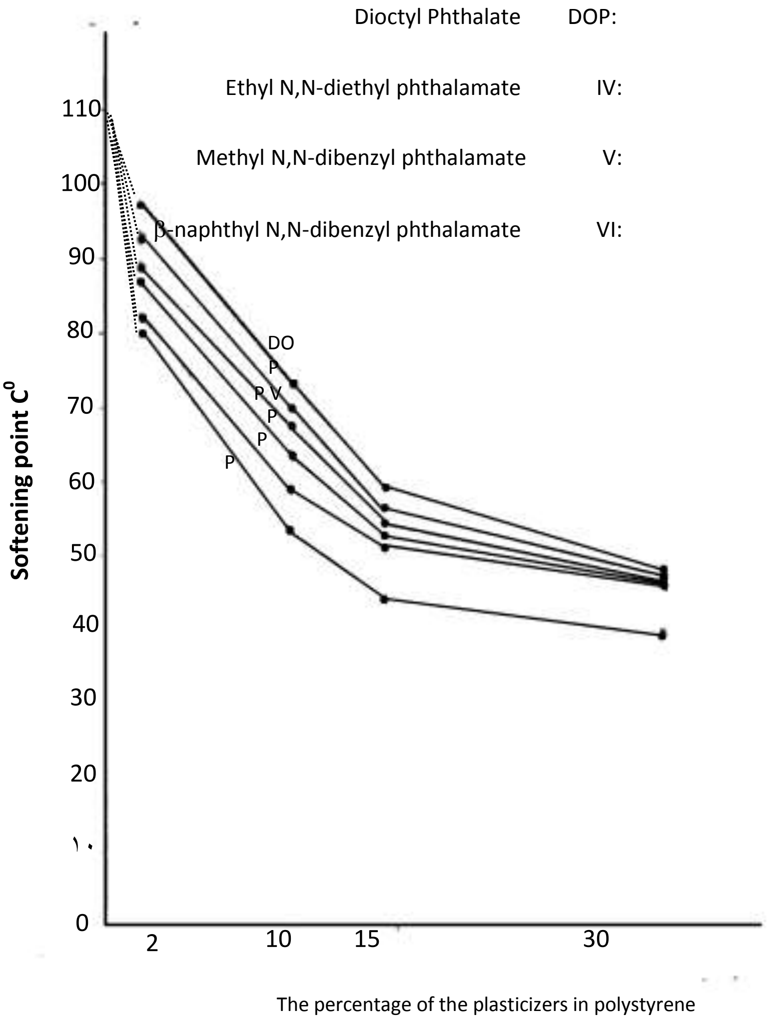

Fig. (2): The effect of the plasticizers to the softening point of polystyrene

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